

Specification for Carbon Steel Materials for Hydrofluoric Acid Alkylation Units

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ABSTRACT

Operation of hydrofluoric (HF) acid alkylation units using primarily carbon steel construction material has been the norm for over 60 years. There have been few problems associated with the use of this material for many years. There have been problems reported within the last 10 years where a non-uniform corrosion phenomenon occurs leading to plant incidents. Residual elements (RE), Cr, Ni and Cu in carbon steel were implicated as a potential cause for this problem. There were inconsistencies though claimed by others or within differing parts of the plant about this RE effect. Galvanic effects were reported that might negate the possible beneficial use of low RE materials. This paper reports the key results of the Joint Industry Project "Materials Specification for HF Alkylation Plant" whose primary objectives were to develop test and corrosion rate measurement procedures for evaluating materials in HF environments and to develop a carbon steel materials specification with respect to the levels of residual elements and carbon in steels for HF alkylation equipment.

INTRODUCTION

The joint industry program managed as a Petroleum Environmental Research Forum (PERF) project began in 1999 with 8 sponsoring companies. The primary objectives were:

- To develop test and corrosion rate measurement procedures for evaluating materials in HF environments.
- To develop guidelines with respect to the levels of residual elements and carbon in steels for HF alkylation equipment.
- To assess the effect of residual elements on weld corrosion in 1% and 60% HF.

A laboratory, was contracted to carry out this specialized work based on laboratory capability dealing with HF and preliminary work on electrochemical techniques for measuring corrosion. This paper summarizes the engineering implications of this work. Details on the experimental procedures and techniques used will be presented in future publications.

In HF alkylation units, dried isobutane and olefins are contacted with nearly anhydrous HF in reactors, in the form of an emulsion, then the acid is allowed to settle leaving about 0.5% of dissolved acid in the reacted hydrocarbon. The settled acid is recycled to the reactors and the hydrocarbon passes to a primary fractionator that removes isobutane and propane as well as the residual acid. The alkylate is collected at the bottom as a liquid, and the remaining hydrocarbons pass to another fractionator where isobutane is collected and recycled. The remaining propane is treated with alumina and KOH to remove organic fluorides and any remaining HF. A simplified flow scheme of a HF Alkylation unit is shown in figure 1.

There are three basic situations where corrosion might be encountered:

- High acid concentration (>90% with water and polymer) found in the reactor section
- Heating or condensing trace acid, which may progress through the azeotropic or constant-boiling concentration of 35.4%, irrespective of the bulk acid concentration in the fractionation section of the plant
- Very dilute acid, ca. 1% formed by the alumina treaters when converting residual HF polymers into water and trace HF.

One might imagine that these would occur sequentially through the plant, but in fact there are a number of ill-defined locations where the azeotropic acid condensate might occur due to boiling or condensing of concentrated acid during fractionation of the hydrocarbons. The main initial interest in this project was in high acid concentrations, most obviously present in the reactor, acid separator (settler) and associated pipework given the high consequence of a leak. The majority of corrosion incidents occur later in the process where the acid concentration in the hydrocarbon is only ca. 0.5%, such as in the depropanizer feed line. Failures have also occurred in the alumina treaters where the high water contents with trace HF are normal.

Many weld corrosion incidents have involved inclusion of silica in the weld metal. This was not considered further. There have been some weld corrosion incidents, which are clear cases of preferential corrosion, and the causes of this were studied in the course of the project.

PHASE I LITERATURE REVIEW

In the first phase of this project, the literature on HF corrosion was reviewed (1-14). It was found that there was remarkably little information of a quantitative nature, and very few laboratory studies showing the influence of residual elements at relevant acid concentrations and temperatures.

The general conclusions from the literature seem to be as follows:

- High residual element (RE) steels corrode preferentially at high acid concentrations.

- Low RE steels often corrode preferentially at low acid concentrations, and invariably do so when galvanically coupled to high-RE steels.
- Laboratory corrosion rates for immersion in low acid concentrations are much higher than any that have been encountered in alkylation plant.
- Weld corrosion effects, other than those associated with dissolution of included silica, are anecdotal, and alloying criteria have not been defined for weld metal.
- Microstructural effects have been neglected.
- Apart from Chirinos, only a Finnish group has used electrochemistry to study HF corrosion, and they abandoned this approach for reasons that were probably invalid.
- The ferrous fluoride scale is claimed to have a thin outer layer in which the iron is in the ferric state. Whilst this is rather hard to rationalize, it may provide an explanation for differences seen as a function of residual elements or microstructure.
- There is some evidence that differences due to RE or microstructure may take effect after a few days of immersion, when the fluoride scale has reached a certain thickness or chemical state.

In addition, a literature review (15-22) of HF solution chemistry was made to determine the impact it may have in relation to plant operations. The main points of interest were:

- Under the conditions used in a HF alkylation plant, the azeotropic acid (35.4%) may not be the main product formed by evaporation/condensation due to pressure drops or temperature differences.
- In fact, at 71°C the more likely equilibrium is between 67% HF in the liquid phase and 97% HF in the vapor phase. (Figure 2)
- Under these conditions, with a significant pressure drop present, the concentrated 99.8% HF is likely to evaporate until a liquid phase HF concentration of 67% is achieved. It could be possible to examine the conductivity of samples taken from the plant to determine the presence of any other dissociated acids within the HF solution.
- Any aromatic molecules in the hydrocarbon mixture present in the alkylation plant could form ionic species in contact with concentrated HF. These could possibly have an effect on the corrosion mechanism.

PHASE II TEST DEVELOPMENT

HF corrosion testing being difficult and relatively limited required building a technique from the ground up. Building on the work of Chirinos (4) it was felt that electrochemical techniques, especially electrochemical impedance spectroscopy (EIS) were the most likely path to success. Testing was to be carried out in both concentrated HF and at the azeotrope HF concentration in Phase II to define the test procedure and conditions needed to test carbon steel element effects in a test matrix.

Tests in concentrated HF were carried out in a 1L Alloy 400 autoclave system fitted with a PTFE liner and equipped to carry out electrochemical corrosion tests in HF up to 99.9% and 95% concentration and any required temperature up to 150°C. This testing revealed that the effects of residual elements in HF alkylation equipment could not be replicated in tests of up to 2 weeks duration in "pure" concentrated acid. The carbon steel materials even with high RE levels underwent a strong passivation reaction. This may explain to some degree why very few cases of non-uniform corrosion have been reported in the concentrated "main acid" sections of the plant. There has been only one case (4) reported here in industry experience.

A PTFE cell (Figure 3) was designed for the ambient pressure tests in azeotropic HF/water mixtures. It had a capacity of 300 ml and was capable of holding up to eight electrodes. This cell also had purging facilities for de-aeration of the solution and the headspace. A PTFE condenser was attached to the top of the cell to avoid any evaporation of the solution. The cell was placed into a thermostatically controlled electric oven to reach the temperature required (71°C). For these Phase II tests, two commercial steels from previous work were used which corresponded to a flange and elbow

that had been exposed in the depropanizer feed line at Amuay Refinery (Venezuela). The flange had high residual elements (0.37%), and the elbow had low residual elements (0.05%). The flange suffered severe corrosion in the plant, while the elbow was relatively uncorroded. The literature review of HF solution chemistry indicated that at 71°C, equilibrium conditions are likely between 67% HF in the liquid phase and 97% in the vapor phase. With a significant pressure drop present, the concentrated 99.8% HF is likely to evaporate until a liquid phase HF concentration of 67% is achieved. Hence tests were conducted in 50%, 60% and 70% HF in order to finalize the test procedure. Plant sample materials provided by the sponsors that give a good range of carbon and residual element concentrations were used. The effect of iron addition was also examined, in an attempt to decrease the time required for the electrodes to reach a stable corrosion rate. An amount of iron filings (5 g/l) were added at the start of the experiment. This approach was successful. Addition of iron at later points in the experiments proved to have a destabilizing effect and was discontinued. It was also found within the preliminary testing that carbon content was an unexpected complication (though not totally unexpected since this is very influential in sulfuric acid corrosion).

PHASE III RESIDUAL ELEMENT TEST MATRIX

Based on the results observed during the Phase II of the project, de-aerated 60% HF (by volume) at 71°C with 5 ppm of pre-dissolved iron was chosen as the test environment for the main matrix of tests. Potential monitoring was undertaken using a continuously immersed pseudo reference electrode. Measurements were also taken against a saturated calomel electrode (SCE) via a sodium fluoride filled solution bridge using small bore PTFE tube with a porous PTFE barrier plug. Bullet electrodes were made where possible, polished to a 1200 grit finish with silicon carbide. The area was usually about 6cm², but could vary from this due to sample geometry and availability.

The sponsors supplied commercial materials in order to be included in the test matrix. They were characterized by composition and microstructure. The steels contained a variety of residual element and carbon levels. These 42 samples taken from operating alkylation plants included examples of corroded and non-corroded base materials and welds, an example of which is shown in Figures 4 (trace acid) and Figure 5 (1% HF). Some of the steels were very similar and since not all could be evaluated in detail, a statistical approach was used to select steels for testing to ensure that firm conclusions could be drawn with respect to the influence of each element on corrosion behavior.

The statistical analysis divided the samples into groups so that selection of one steel from each group would give the best coverage of the whole composition range of each element of interest. The samples were selected using a "spacefilling" criterion. The microstructures of all the samples were very similar, therefore this was not considered as a variable.

For statistical analysis it was initially decided to include 15 different materials in the 60% test matrix to assess the effect of C, Cu, Ni and Cr on corrosion behavior. However, weld samples and other samples of interest to the sponsoring group eventually increased the number to 21.

Phase III Results

The EIS response on a Nyquist diagram was normally of the form of a single semicircle, from which could be obtained the resistance and capacitance of the corroding interface. The corrosion rate can be obtained from the polarization resistance associated with the corrosion process.

Where general categorization of materials has been undertaken in terms of residual element and carbon concentration the definition is as follows:

Residual elements 0 - 0.15% = low, 0.16% - 0.30% = medium, ≥0.31% = high

Carbon 0 - 0.10% = low, 0.11% - 0.20% = medium, ≥0.21% = high

This is a definition giving a reasonable reflection of the spread of materials examined. It does not relate to the 0.2% residual element criterion proposed by Hashim and Valerioti (Ref 9).

It should be noted that while the corrosion rates are relatively stable in the later period of the experiment, the rest potentials of the electrodes are not. Substantial movement in rest potentials (10's of mV) occurred even though corrosion rates show little change. As will be discussed later, this is an indication of strong diffusion control of the corrosion reaction. While all the samples show a pseudo-passivation, with protective film formation and relatively low longer term corrosion rates, some samples are capable of undergoing a much stronger passivation, with very low corrosion rates obtained. While this does not happen for every sample of a given material examined, it was found that all the materials capable of showing this behavior were low RE with moderate to high carbon levels. The averaged normalized triplicate (or greater) long term corrosion rates for the full matrix of materials examined are presented in Figure 6.

A number of observations are immediately evident. The first observation is that from the 21 materials examined, the eight materials with the lowest corrosion rates are all low RE materials. The second observation is that the five highest corrosion rate samples are all moderate/high RE. This gives some initial support to the concept of a strong RE effect. This would mirror the trends seen in industry with higher concentration HF environments. Also, the lowest corrosion rate materials corrode at about 25% of the rate of the highest corrosion rate materials. This implies that a substantial improvement in plant component lifetime could therefore theoretically be obtained by correct selection of low RE materials.

Figure 7 shows a three dimensional surface graph of the data, obtained by the Origin matrix expansion technique. The graph should be regarded as a trend indicator and not as an absolute definition or predictor of corrosion behavior for a specific material. Some metals of very similar carbon and residual element concentrations can show substantial variation in their measured corrosion rate.

There are three general zones of residual element behavior. There is a region below 0.1 wt % RE where the lowest corrosion rates are observed. As the RE content increases towards 0.25% there is a steep slope of increasing corrosion rate. Beyond this value there is a region with higher corrosion rates. The results generally support the concept of a maximum RE criterion often used in materials selection for HF alkylation equipment. Generally, below 0.2% RE, lower corrosion rates are obtained compared to above this value. However, it is also clear that in the environment examined, 0.2% RE is towards the top of the sloping section of the surface. The implication is that a 0.15% RE criterion in materials selection should lead to better performance and may explain why the 0.2 wt% criteria may have some field inconsistencies.

At low RE concentrations there is also clearly a beneficial carbon effect. The best general performance is implied from the low RE high carbon corner of the graph. As described previously, the materials in this region are the only ones capable of giving very strong passivation, producing extremely low corrosion rates. It may well be that a similar passivation, occurring over a much longer period, underlies the RE effect in plant over the whole range of C contents. The recommended carbon concentration indicated by these results would appear to be 0.18% or greater, although with increased exposure time the passivation phenomena may move to include more moderate carbon concentrations.

Comments from the sponsors indicate that historically, plants would have been built predominantly from materials in the low RE-high C corner of the diagram. However, in recent years there has been a tendency to move to lower carbon materials with more recycled content and thus higher RE levels. These materials sit in the region diametrically opposite to the low RE-high C corner, and the suggestion from this work is that these materials should be less resistant to corrosion. The sponsors have experienced an increased tendency for problems in recent years, and this trend in material chemistry could possibly explain this phenomenon. These observations are useful in explaining some of the failures observed in the samples provided by the sponsors.

The relatively simple analysis discussed above was based on a comparison of carbon and combined residual element content. In order to evaluate the effects of the individual residual elements, statistical analysis of the corrosion rate results was conducted. The relative individual effects of carbon and the residual elements copper, chromium and nickel were assessed. The conclusions of this examination are given below.

- A simple first order analysis of the data gave a poor statistical fit for all of the elements examined, indicating that individual elements on their own do not have a strong influence on the corrosion rate.
- A full second order response surface regression analysis of corrosion rate dependence on carbon, copper, nickel and chromium content gave a good fit to the data, with 80% of variation explained by the fitted model.
- The minimum corrosion rate implied by this fitted model is achieved by setting carbon content and chromium content at their maximum values (0.25% used here), with copper and nickel set to zero.
- This would imply that combinations of two or more elements strongly affect corrosion rate, with the combined presence of copper and nickel being especially detrimental.
- However, this is not a simple conclusion. Contour plots derived from this fitted model show a saddle point, rather than a simple maximum or minimum, suggesting that great care is needed with respect to the combination of these elements, particularly the residual elements, when trying to minimize corrosion.
- In simple terms, no one residual element on its own has a dominant effect on the corrosion rate. Two or more elements act together to affect corrosion rate. The presence of significant levels of both copper and nickel in the same material appears to be especially detrimental for the corrosion rate. The results suggest that carbon is generally beneficial, but can be detrimental in higher RE materials with high Ni content. Chromium appears to be neutral or even beneficial at high carbon concentrations, but becomes detrimental as the carbon concentration decreases.
- However, the interactions between these elements (C, Cu, Ni, Cr) are very complex.

Phase III Conclusions.

Overall, the results support a maximum residual element (RE) criterion (where the RE content is based on the wt % summation of nickel, chromium and copper content), although a reduction from the industry guideline value of 0.2% to 0.15% would be beneficial if this is practical in terms of materials supply. There is a strong beneficial effect of carbon in low RE materials. This could explain the greater incidence of failures in recent years due to use of modern low carbon steels. It could also explain some anomalous results in relation to the 0.2% alloying criterion. From this work a carbon concentration of 0.18% or greater is recommended. From the above conclusions it is considered that if the minimum carbon recommendation is met for a given material, then chromium can be excluded from the maximum RE requirement. However, if the minimum carbon recommendation is not met then chromium should be included in calculating the total RE value.

Galvanic effects were also examined in Phase III 60% HF. It was found that between the various metals examined in this environment, galvanic effects of the majority of samples were less than 10% of the measured corrosion rate, although occasionally couples, including weld materials or electrodes with a large potential difference, can reach a galvanic current of 40% of the measured corrosion rate. However, this is based on electrodes of approximately equal size. If an electrode area ratio of 10:1 or 100:1 is assumed, then galvanic effects may become much greater. The relative areas involved in any galvanic couple would be important. However, since all the corrosion rates in 60% (and more concentrated) acid are in some way diffusion controlled, extreme galvanic effects are not expected in these environments.

PHASE III. TESTING OF RESIDUAL ELEMENT IMPACT IN DILUTE HF

There have been several anomalous plant corrosion failures due to RE in the alumina treater portion of the plant. Specifically, it appears that low RE material corrodes locally at higher rates particularly when coupled to a high RE component. In order to compare the corrosion behavior with that in 60%HF, eight materials including those showing the highest and lowest corrosion rates in the 60% environment were tested in 1%HF at 40°C. The tests were carried out in a de-aerated 1% HF

solution for eight days, with no agitation and under uncoupled conditions. Eight samples from the original test matrix that represented the highest and lowest corrosion rates were used in these tests. The tests were done in duplicate and were reasonably reproducible.

This testing showed that in general the low RE materials generally presented a more negative potential than the high RE materials. This systematic potential difference between low and high RE materials confirms that the main issue in the 1% HF environment is galvanic effects, which is not evident in uncoupled conditions. In order to study the galvanic effect in 1%HF, some work was carried out coupling the samples at the beginning or at the end of the test. The effect of agitation was also studied.

The samples that were coupled together from the beginning of the test showed preferential galvanic corrosion of the low RE material. Figure 8 shows the contribution of the galvanic current to the corrosion rate of the low RE material coupled to the high RE material. (In this figure, "1st test" refers to the situation without agitation, and "2nd test" refers to the situation with agitation). It is shown that there is a strong galvanic effect tending to corrode the low RE material preferentially.

This observation was then confirmed by testing a sample (seen in Figure 4) from a sponsor's plant where the low RE reducer preferentially corroded when coupled to the high RE pipe and tee. The coupled samples showed preferential galvanic corrosion of the low RE material, producing galvanic currents as high as 600 $\mu\text{A}/\text{cm}^2$ after 2 days immersion. This represents a galvanic contribution of more than 7 mm/yr to the corrosion rate (i.e. essentially all of it is galvanic and the low RE material is more-or-less a pure anode).

PHASE IV. WELDMENTS

Though the Phase III tests confirmed that RE has the same role in either base metal or weldments, there have been concerns that welds represent a potential risk for galvanic effects and preferential corrosion. Preferential weld corrosion has been reported in service in both the 60% and 1% acid regime. Hence testing was undertaken in these two environments to determine if welds galvanically interacted with base metals to cause a different corrosion response over and above the RE effects. Testing of welds individually and galvanically coupled were done in both the 1%HF and 60% HF environments similar to that reported for the base metals in this paper. The details of the experimental work on as received plant samples and welds manufactured for the program will not be presented in this paper.

The conclusions that could be made from this testing are:

Based on these results in 60% HF at 71°C, it was concluded that:

- There was no different effect for welds contributing to preferential corrosion other than the RE effects outlined in the Phase III matrix.
- The corrosion rate for 7018 was 1.5-2 times lower than 6010.
- Post Weld Heat Treatment did not seem to cause a significant effect in the corrosion resistance, except by one test carried out in the 7018 low RE material, which passivated after 2 days immersion.
- Galvanic effects were complex and showed no clear effect of PWHT.

Based on these results in 1% HF at 40°C, it was concluded that:

- The difference in RE content between the filler electrode materials did not cause any effect on the corrosion resistance.
- The uncoupled corrosion rates for 7018 was significantly lower than 6010.
- Galvanic effects were complex. However, The 6010 material tended to show increased galvanic currents when coupled to high RE material. A possible reason for the difference is that the 6010 microstructure in particular may contain segregated regions that are more anodically active.
- PWHT samples were not tested in 1% acid due to project constraints.

PHASE IV. SEM EXAMINATION

Surface and cross-sectional SEM studies were carried out on ferrous fluoride films developed during immersion of steel samples in 60% HF solution. Two microscopes were used: a conventional Amray system equipped with EDX including light-element analysis, and a state-of-the-art field emission gun unit (FEG-SEM).

Many things might have been determined from these examinations. For example, residual elements or their oxides might have accumulated at the metal/film interface, leading to loss of film adhesion and/or destruction of the coherent film morphology. Similar accumulation might have occurred at grain boundaries within the film. Residual elements such as Cu and Ni that accumulate in the metallic state might have catalyzed the cathodic reaction of hydrogen evolution. Finally, the residual elements might have altered the transport properties of the film by a doping effect (although it would not be right to think of this as analogous to high-temperature oxidation, since the film forms by a process involving a lot of water and dissolution-reprecipitation).

In fact, all the above possibilities remain just that – possibilities. Despite detailed SEM examination, any enrichments of alloying elements remain too subtle for us to detect. However, much useful information has been obtained on the fluoride films and their mode of formation. Enhanced film detachment has been observed in high-RE alloys.

Two materials were selected that showed a classical RE effect. The samples were immersed in 60% HF at 71°C for a longer period of time (35 days) in order to develop a good fluoride film, suitable for examination in the SEM. The samples were medium-carbon low and high RE. The corrosion rate difference between these two specimens was two times. Figures 9 and 10 are SEM photographs of the high RE sample and low RE sample respectively. As it can be immediately seen the film on the low RE sample is much thinner than the high RE sample. The differences in film thickness were as expected from the electrochemical corrosion rate measurements. Both films start with a coarse porous outer layer that is formed in the first 1-2 days of exposure. The balance of the film is a dense low porosity fluoride film. The film morphologies were different, but only subtly so. No important segregation of residual elements was detected in any of the following measurements:

- Metal surface after film detachment
- Under-surface of film after detachment.
- Cross-section of film after fracture.

The only important differences that were obtained were:

- Easier detachment of the film on the high RE material (more metallic surface left under the film).
- Copper present on the top of the high RE film.

The former observation appears significant but could not be analytically supported with this technique. The copper enrichment is not thought to be causally related to corrosion, though it is an interesting observation. It is difficult to see what copper could do on the outer surface that would affect corrosion. We believe there is alloying element enrichment at the metal-film interface, but in too thin a layer to be detected by EDX.

The residual elements were at the limit of detection, and as far as could be determined were not concentrated in any particular region; they were detectable all the way across the film.

Images were obtained from the underside of the detached film and from the opposing surface, which may or may not be the clean metal surface. These led to the following observations (1) the low RE material showed an optically dark metal surface indicative of adhering film material, and (2) the high RE material generally showed a bright metal surface with evidence of local chemical polishing (typical of corrosion under a salt film). This interface did not show, on either side, concentrations of residual elements significantly higher than their bulk levels.

In summary, the SEM analyses showed that the fluoride films formed in HF environments are truly remarkable materials, but did not reveal precisely why they are different in low and high RE materials.

The most likely reason must be that there is a subtle doping effect that enhances the ionic conductivity of the high-RE films.

CONCLUSIONS

The primary conclusions of this study are summarized below.

- Laboratory test procedures for evaluation of corrosion in concentrated HF environments have been developed. The benefits of using electrochemical techniques have been demonstrated. The use of electrochemical impedance using a nickel/nickel fluoride reference electrode is recommended for use in highly concentrated HF environments.
- The residual element effects observed in HF alkylation equipment cannot be replicated in short term tests in "pure" concentrated acid. This environment is too passivating.
- Corrosion problems in areas of HF alkylation units handling strong acid are considered to be due to:
 - i. The presence of impurities other than water in the concentrated HF, and/or (not significantly tested in this program.)
 - ii. The presence of water at locally high concentrations.
- Consideration of the HF solution chemistry indicates that under significant pressure drop conditions, concentrated HF is likely to evaporate to a liquid phase concentration of 67% and hence scenario (ii) above is viable.
- Tests in 60% HF at 71°C has been shown to reflect the residual element effects observed in service.
- Combinations of copper and nickel have the most detrimental effect on corrosion of steels in "concentrated" HF. Carbon appears to be beneficial, except in combination with high nickel content. Chromium appears to be neutral or even beneficial at higher carbon levels, but may become slightly detrimental as the carbon concentration is reduced.
- Overall, the results support a maximum residual element (RE) criterion (where the RE content is based on the wt % summation of nickel, chromium and copper content), although a reduction from the industry guideline value of 0.2% to 0.15% would be beneficial if this is practical in terms of materials supply.
- There is a strong effect of carbon, particularly in low RE materials. This could explain the greater incidence of failures in recent years due to use of modern low carbon steels. It could also explain some anomalous results in relation to the 0.2% alloying criterion. From this work a carbon concentration of 0.18% or greater is recommended.
- From the above conclusions it is considered that if the minimum carbon recommendation is met for a given material, then chromium can be excluded from the maximum RE requirement. However, if the minimum carbon recommendation is not met then chromium should be included in calculating the total RE value.
 - For base metals the optimum specification would be **$C > 0.18 \text{ wt\%}$** and **$Cu + Ni < 0.15 \text{ wt\%}$** .
 - For weld metals the specification should be (where C levels are lower) **$Cu + Ni + Cr < 0.15 \text{ wt\%}$**
- Studies on coupled materials and weldments have shown that in 60% HF, corrosion is dominated by diffusion effects through the fluoride film. Hence, galvanic effects are expected to be less significant in this and more concentrated HF environments.
- There are no clear effects with respect to RE content on the corrosion of uncoupled steels in dilute (1%) HF.
- Studies on coupled materials and weldments have shown that low RE material will corrode preferentially when in contact with high RE material in 1% HF.

- The 7018 weld filler metal has a superior corrosion resistance in comparison with 6010 in both 1% and 60% HF.
- Post weld heat treatment does not provide any significant benefits in relation to corrosion behavior in the HF environments studied.
- RE in itself will not mitigate corrosion in systems that are known to be corrosion prone due to exposure through the corrosive acid regimes. This work has demonstrated that HF corrosion is strongly affected by steel composition and that localized corrosion rates can be subtly affected by local chemistry differences.
- There is still uncertainty as to the possible impact of contaminants found in operating plants that may impact the corrosivity of the HF. This may be a wild card that may also impact the response of carbon steel in some plants while not in others. A proposal for further work in this area is being offered for a second phase study in better understanding HF acid corrosion to carbon steel.

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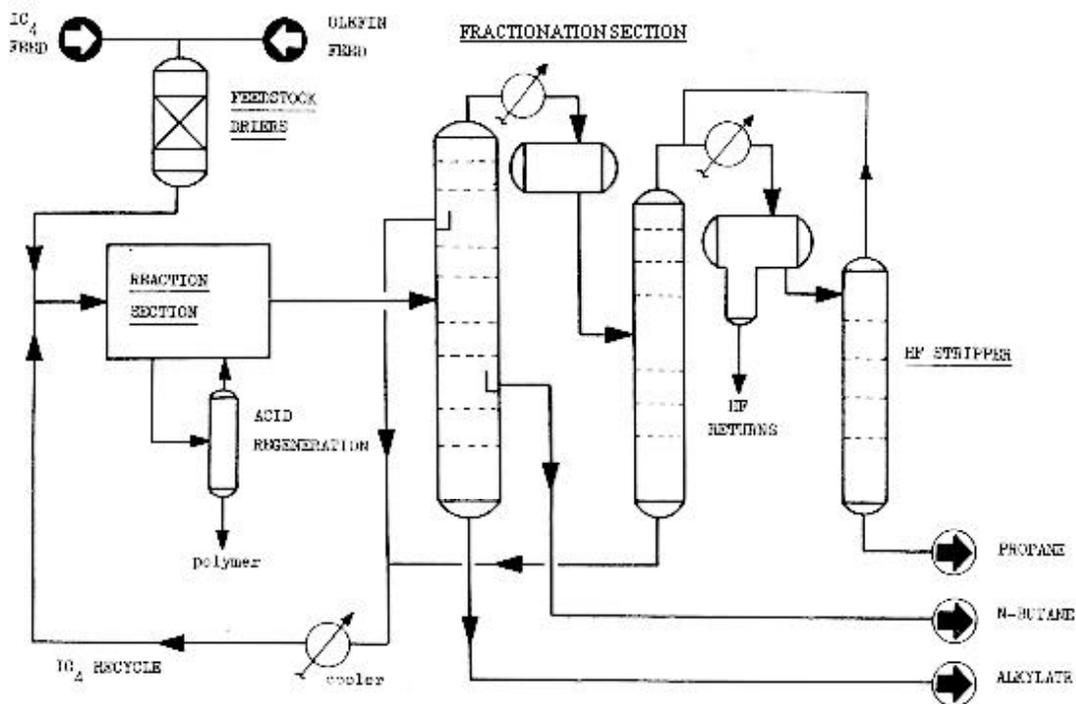


Figure 1. Generic flow scheme of a HF Alkylation plant.

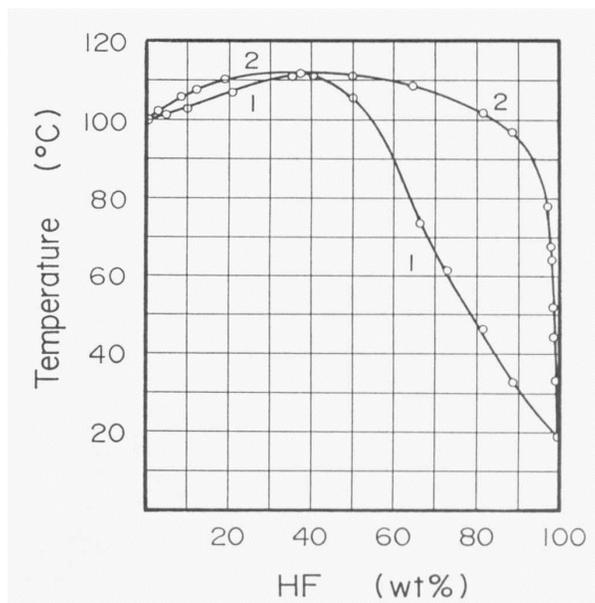


Figure 2. Boiling points and vapor-liquid composition of the binary system HF-H₂O. 1, Liquid phase; 2, vapor phase.[15]



Figure 3. PTFE cell fitted with a PTFE condenser for ambient-pressure electrochemical studies.



Figure 4. Example of sponsor supplied sample for Phase II Matrix testing (Trace HF).



Figure 5. Example of sponsor supplied sample for Phase II Matrix testing (1% HF).

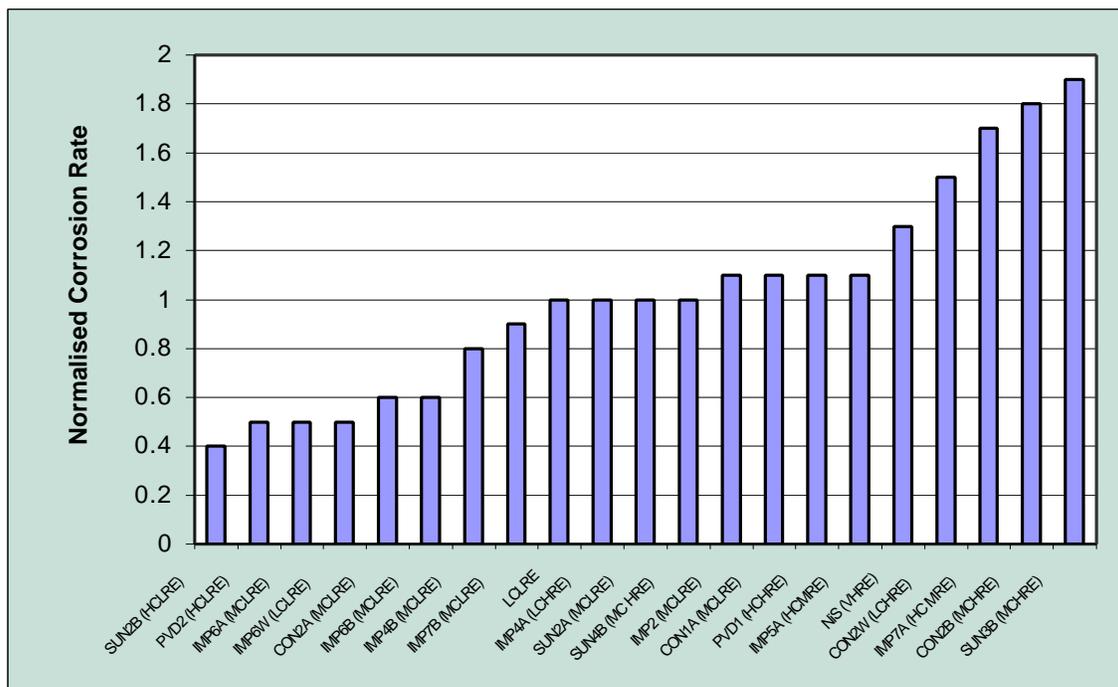


Figure 6. Normalized stable corrosion rates in 60%HF/71°C at day 14-15, including weld materials.

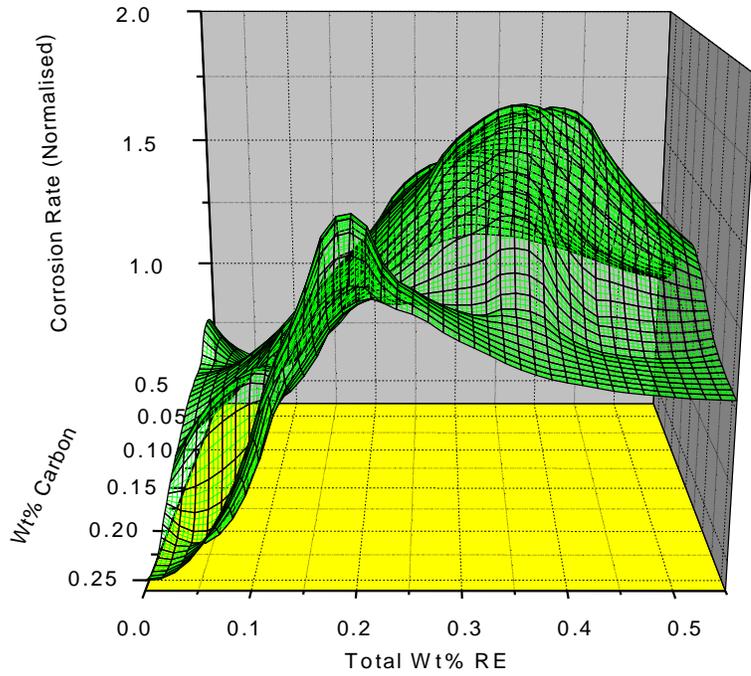


Figure 7. 3-D surface graph of corrosion rate data obtained in 60%HF/71°C, including weld materials.

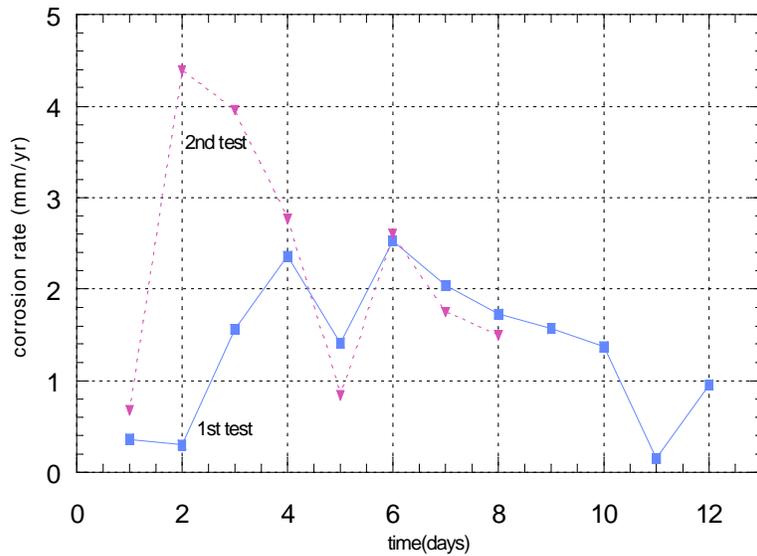


Figure 8. Contribution of the galvanic current to the corrosion rate of the low RE material coupled to the high RE material.

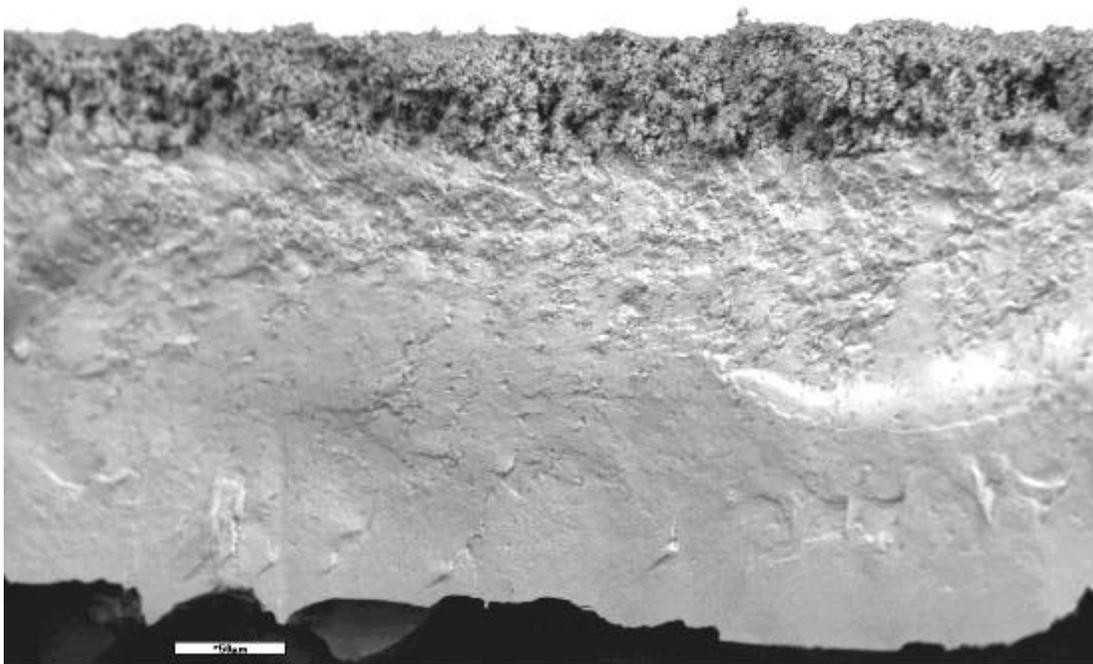


Figure 9. Fracture section of the thick film developed on the high RE material. (note scale is 50µm)

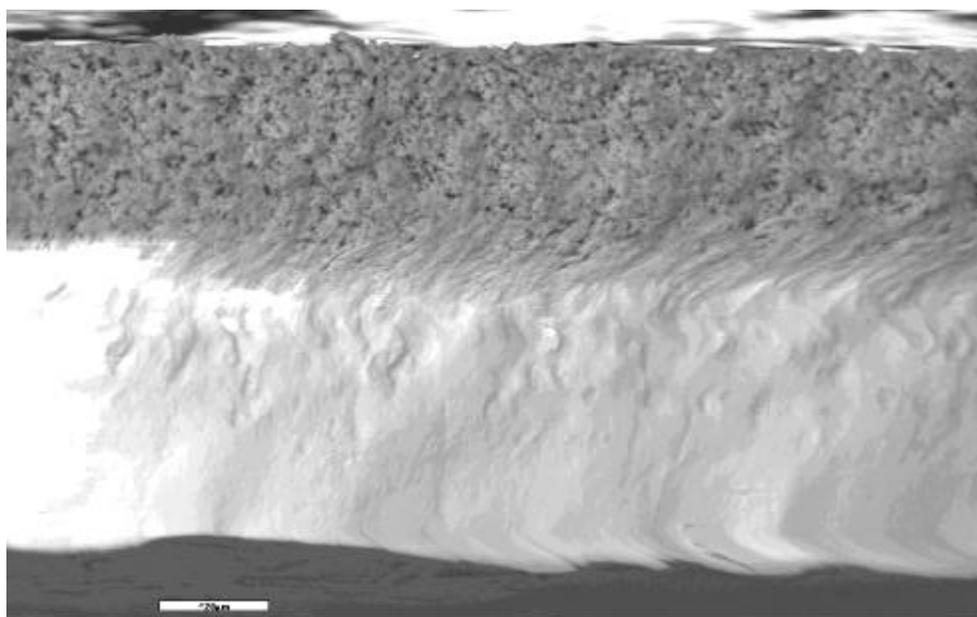


Figure 10. Fracture section of the thin film developed on the low RE material. (Note higher magnification 2.5 x then Figure 8.)